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Mechanical properties of tricalcium phosphate-fluorapatite-alumina composites

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Abstract

This study deals to produce tricalcium phosphate - fluorapatite composites sintering at various temperatures (1300°C, 1350°C and 1400°C) and with different alumina additives amounts (2.5 wt%, 5 wt%, 7.5 wt%, 10 wt% and 20 wt%). The characterization of samples before and after sintering was investigated, using X-ray diffraction, infrared spectroscopy, scanning electronic microscopy and by analysis using ^{31}P and ^{27}Al nuclear magnetic resonance. Mechanical properties have been measured by Brazilian test. The evolution of composite rupture strength was studied as a function of sintering temperature. The effect of sintering on the mechanical properties was measured with the change in composition and microstructure of the composite. The mechanical resistances of composites were increased with the temperatures and with concentrations of alumina. At 1350°C, the mechanical resistance reaches its maximum value with 5 wt % Al_2O_3 (13.6 MPa) whereas the optimum density is about 90 % with 2.5 wt % Al_2O_3 .

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Keywords: Biomaterial, Alumina, Sintering, Composites, Mechanical Properties.

1. Introduction

Phosphate calcium based materials have attracted considerable interest for orthopaedic and dental applications [1-4]. But their usage at high load bearing conditions was restricted due to of its brittleness, poor fatigue resistance and strength [4-5]. In fact, the majority of bioceramics have low mechanical properties such as hydroxyapatite, tricalcium phosphate (β -TCP), fluorapatite (Fap) [1-17]. In this study we have use the commercial tricalcium phosphate (β -CTCP) and the fluorapatite (Fap). β -CTCP favour bone reconstruction, thanks to height restorability due to their biocompatibility and bioactivity/restorability but it has poor mechanical resistance [4, 9-14]. Fap has been used due to of its higher stability and its better mechanical properties than tricalcium phosphate [4, 11, 13]. Many researchers have also demonstrated that fluoride ions in the culture medium stimulated osteoblastic activities in terms of cell proliferation and differentiation [4, 7]. Fap has been used with a fixed 26.52 wt% amount because the human bone contains 1 wt% of fluorine approximately [15-16].

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Bioinert ceramic oxides like alumina (Al_2O_3) having high strength is used to enhance the mechanical properties of CTCP - Fap composites. Alumina has been used in the biocomposite for its biocompatibility and its better stability and mechanical properties than β -CTCP and Fap [15, 18-19]. The CTCP-26.52 wt% Fap composites have excellent biocompatibility but its poor mechanical properties which restrain its applications. Therefore, effort must be made to ameliorate densification and mechanical resistance of CTCP-26.52 wt% Fap composites. We have try to optimise much parameters; weight of Al_2O_3 and sintering temperatures were optimise in order to elaborate CTCP-26.52 wt% Fap composites which have acceptable properties: density and mechanical propriety.

2. Materials and methods

In order to elaborate CTCP-Fap- Al_2O_3 composites material, we used commercial tricalcium phosphate (Fluka), synthesized Fap and Al_2O_3 (Fluka) powders. The Fap powder was synthesized by precipitation method [6]. A calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Merck) solution was slowly added to a boiling solution containing diammonium hydrogenophosphate ($(\text{NH}_4)_2\text{HPO}_4$, Merck) and ammonium fluorine (NH_4F , Merck), with continuous magnetic stirring. During the reaction, pH was adjusted to the same level (pH 8-9) by adding ammonia. The obtained precipitate was filtered and washed with deionised water; it is then dried at 70°C for 12 hours. Calculated quantities of each powder (β -CTCP-Fap- Al_2O_3) were mixed and milled with absolute ethanol and treated by ultra-sound machine for 15 minutes. Cylindrical tablets were produced by inserting 4 g of powder into a 20mm diameter die and uniaxially compacting under a load of 47.1 kN (at pressure of 150 MPa). Finally the compacts discs were sintered at various temperatures (1300°C ; 1350°C and 1450°C). The heating rates were $10^\circ\text{C}/\text{min}$.

The received powder was analyzed using X-ray diffraction (XRD). The X-rays have used the Seifert XRD 3000 TT diffractometer. The X radiance was produced by using CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$). The crystalline phases were identified by reference to the ICCD files. ^{31}P and ^{27}Al Nuclear magnetic resonance (MAS-NMR) spectra were run on a Bruker 300WB spectrometer. The ^{31}P and ^{27}Al observational frequency were 121.49 MHz and 78.2 MHz, respectively. ^{31}P shift are given in parts per million (ppm) referenced to 85 wt% H_3PO_4 . The ^{27}Al NMR chemical shifts were referenced to a static signal obtained from an aqueous aluminium chloride solution. The microstructure of the sintered compacts was investigated by scanning electron microscopy (SEM Phillips XL 30) on fractured sample surfaces. Differential thermal analysis and thermomechanical analyses are carried out using about 20 mg of powder in Argon (DTA-TGA and TMA; Model Setaram). The heating rate is $10^\circ\text{C min}^{-1}$.

The particle size dimension of the powder was measured by means of Micromeritics Sedigraph 5000. The specific surface area (SSA) was measured by the BET method using azotes (N_2) as an adsorption gas (ASAP 2010) [20]. The primary particle size (D_{BET}) was calculated by assuming the primary particles to be spherical [8]:

$$D_{\text{BET}} = \frac{6}{s \cdot \rho} \quad (1)$$

where ρ is the theoretical density of β -CTCP (3.07 g.cm^{-3}), Fap (3.19 g.cm^{-3}) or Al_2O_3 (3.98 g.cm^{-3}) and S is the SSA.

Mechanical properties of the compacts have been measured by Brazilian test. The maximal rupture strengths σ_r is given by equation [13, 17, 21, 22]:

$$\sigma_r = \frac{2 \cdot F}{\pi \cdot D \cdot e} \quad (2)$$

where F is the tensile strength and D and e are the diameter and the thickness of the sample.

3. Results and discussion

3. 1. Sintering of β -CTCP-26.52%Fap-alumina composites

The SSA of β -CTCP, Fap, alumina and β -CTCP-26.52%Fap composites are 0.8, 29, 2.87 and 3 m²g⁻¹, respectively. Table 1 summarizes the DTA measurements, sintering domain and characteristics of different powder used in this study. The DTA analyse prove that β -CTCP, Fap and alumina present an endothermic peaks. Fap's analyse prove the presence of a binary eutectic between CaF₂ and Fap was observed at 1180°C. Two endothermic peaks were relative to β -CTCP and β -CTCP-26.52%Fap composites wich due to the two allotropic transformations: β to α (at 1290°C and 1280) and from α to α' (at 1464 and 1444°C). Large sintering domain was observed for the three powders. This variation of the sinterability is relative to the difference between physicochemical compositions of those powders.

Table 1. SSA, average grain size obtained by different analysis, DTA measurements and sintering domain of different powder used in this study.

Powder	SSA (m ² /g)	D _{BET} (μ m)	D ₅₀ (μ m)	DTA measurements (endothermic peak) (°C)	Sintering domain (°C)	d ^(a)
Fap [8]	29.00	0.07	6	1180 (liquid phase)	715-1100	3.19
β -CTCP	0.80	2.40	5	1290 ($\beta \rightarrow \alpha$) 1464 ($\alpha \rightarrow \alpha'$)	1100-1300	3.07
Al ₂ O ₃	2.87	0.53	3	-	1400-1600	3.98
Composites ^(b)	3.00	0.64	-	1280 ($\beta \rightarrow \alpha$) 1444 ($\alpha \rightarrow \alpha'$)	1100-1250	3.10

^(a)Theoretical density. ^(b) β -CTCP-26.52%Fap composites.

The experiment was carried out on some samples containing different weight ratio of alumina (2.5 wt%, 5 wt%, 7.5 wt%, 10 wt% and 20 wt%) sintered at various temperatures (1300°C, 1350°C and 1400°C). Fig. 1 shows the results of relative density of β -CTCP–26.52 wt % Fap-alumina composites. The ultimate densification was obtained at 1400 °C with 2.5 wt% Al₂O₃ (90%) and the minimum densification is approached at 1300 °C with 20 wt% Al₂O₃ (Fig. 1). The densification of the biomaterial increases with sintering temperature. In fact, we observe that relative density was lower than samples which were sintered at 1350°C and 1400°C. Fig. 2 shows the mechanical properties evolution of β -CTCP-26.52%Fap-Al₂O₃ according to the sintering temperature. At 1350°C the rupture strength reaches maximum 13.5 MPa when 5 wt% Al₂O₃ are added. We register low rupture strength when samples were sintered at 1350°C. Densification was driven by mush parameters and phenomena. In fact when powders do not have similar size and different chemical nature mush driving force and phenomena will appears. The difference of temperatures fusion and start densification of different start powder conduce at the fluctuation of the results of the sintering process and all those phenomena will modify the densities of the specimens and mechanical resistance. Alumina height sintering temperature conduct to the increase of temperature sintering (1350°C for composite without alumina to 1400°C with alumina) but we attain best mechanical and densification for samples containing alumina than samples without alumina.

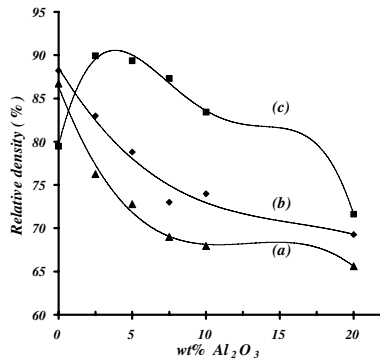


Fig.1. Relative density of β -CTCP-26.52wt%Fap composites sintered with different percentages of alumina at: (a) 1300 °C; (b) 1350 °C; (c) 1400 °C.

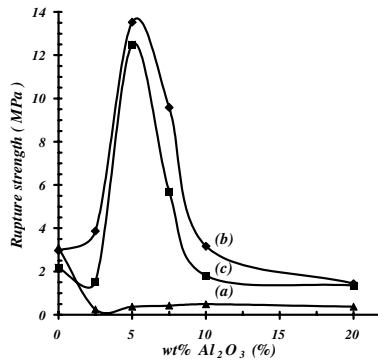


Fig.2. Rupture strength of β -CTCP-26.52wt%Fap composites sintered with different percentages of alumina at: (a) 1300 °C; (b) 1350 °C; (c) 1400 °C.

3. 2. Characterization of sintered samples

The Characterisation of sintered samples were tested, using Fourier Transform Infra Red spectroscopy (FTIR), X-ray diffraction (XRD), scanning electronic microscopy (SEM) and by analysis using ³¹P nuclear magnetic resonance.

The XRD patterns of composites sintered at 1400°C without and with different percentages of alumina (2.5 wt %, 5 wt %, 7.5 wt % and 20 wt %) were shown in Fig. 3.

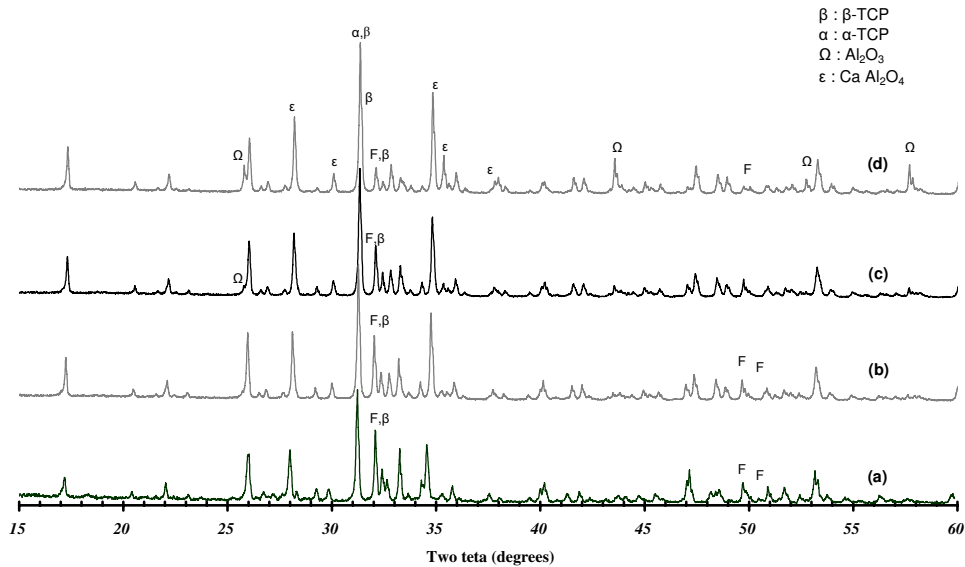
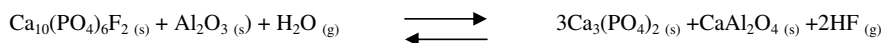


Fig. 3. XRD patterns of β -CTCP-Fap composites sintered at 1400°C with different percentages of alumina: (a) 0 wt%, (b) 5 wt%, (c) 7.5 wt%, (d) 20 wt%.

The XRD patterns of β -CTCP-26.52wt% Fap sintered with different percentages of alumina (2.5 wt%, 5 wt%, 7.5 wt% and 20 wt%) show the presence of Fap, β -CTCP and Al_2O_3 (Figs. 3a–c). The samples sintered at 1400 °C with 20 wt% Al_2O_3 show in more the presence of traces of α -TCP and CaAl_2O_4 phases (Fig. 3d). At 1400°C the Fap peaks decreases when the percentage of alumina increases. This result confirms the partial decomposition of Fap when the concentration of alumina increases. At 1400°C, the reaction of Fap with alumina is probably explained as follows:



The presence of CaAl_2O_4 is also probably produced by solid reaction between Al_2O_3 and CaO , which is explained as follows:



CaO is produced by solid reaction between CaF_2 and H_2O [8]. The similar reactions were observed also by Ben Ayed et al. and Kim et al. [15, 19].

The FTIR spectra of CTCP-26.52% Fap composites sintered at various temperatures (1350°C and 1400°C) without or with alumina addition are shown in Fig. 4. The bands at 3467 and 634 cm^{-1} corresponded to the water absorption band. FTIR spectra indicate the presence of vibration bands corresponding to the presence of phosphate groups bands at 550, 604, 942-962, 1034 and 1134 cm^{-1} and alumina bands at 490, 463 and 648 cm^{-1} and (Fig. 4). The pyrophosphate bands (at 700 cm^{-1} and 1200 cm^{-1}) decrease with temperature and with percentages of alumina. However, the result confirms the interaction between pyrophosphates with tricalcium phosphate above 1278°C [10].

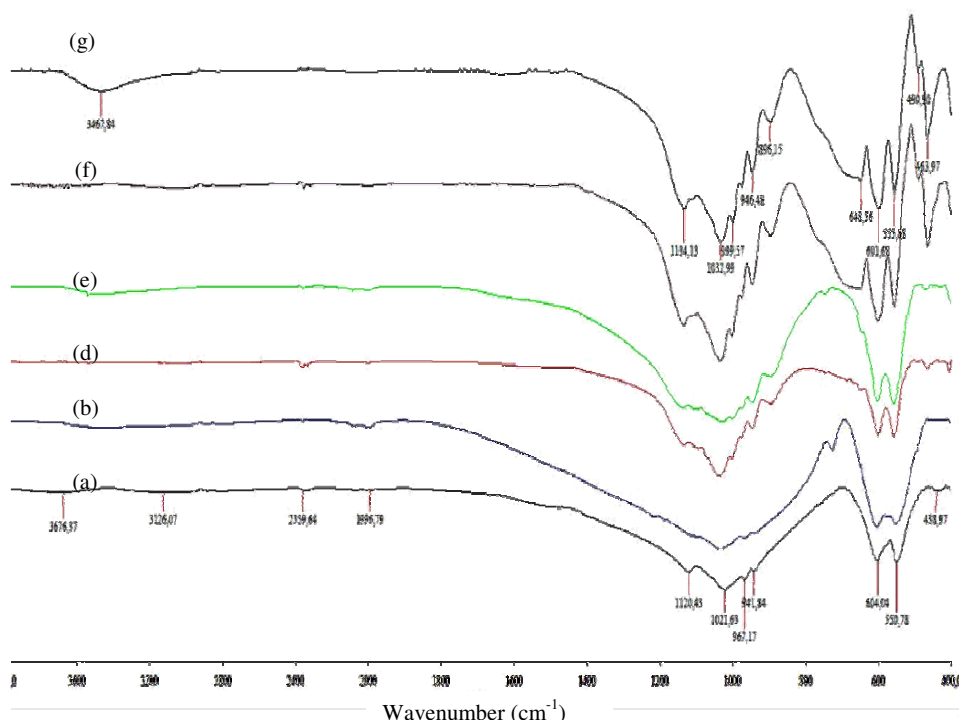


Fig. 4. IR spectra of CTCP-25.265%Fap sintered without and with different percentages of alumina at various temperatures: (a) 1350°C, (b) 1400°C, (d) 5 wt%-1350°C, (e) 5 wt%-1400°C, (f) 20 wt%-1350°C and (g) 20 wt%-1400°C.

Fig. 5 shows S.E.M micrographs of the β -CTCP (fracture surfaces) sintered at various temperatures (1350°C and 1400°C) with different percentages of Al_2O_3 (2.5 wt% and 20 wt%). Fig. 5a, 5b show the microstructural developments of CTCP-26.52wt%Fap sintered without alumina at various temperatures (1350°C and 1400°C). The macrographs of the rupture facieses present continuous phases in addition the formed spherical pores prove that a liquid phase was formed at 1400°C (Fig. 5b). In Fig. 5c-5h, the samples present an important intergranular porosity with presence of spherical pores when samples were sintered at 1350°C and 1400°C with 20% Al_2O_3 . In addition we have a small size grain relative to alumina (Fig. 5c-5h).

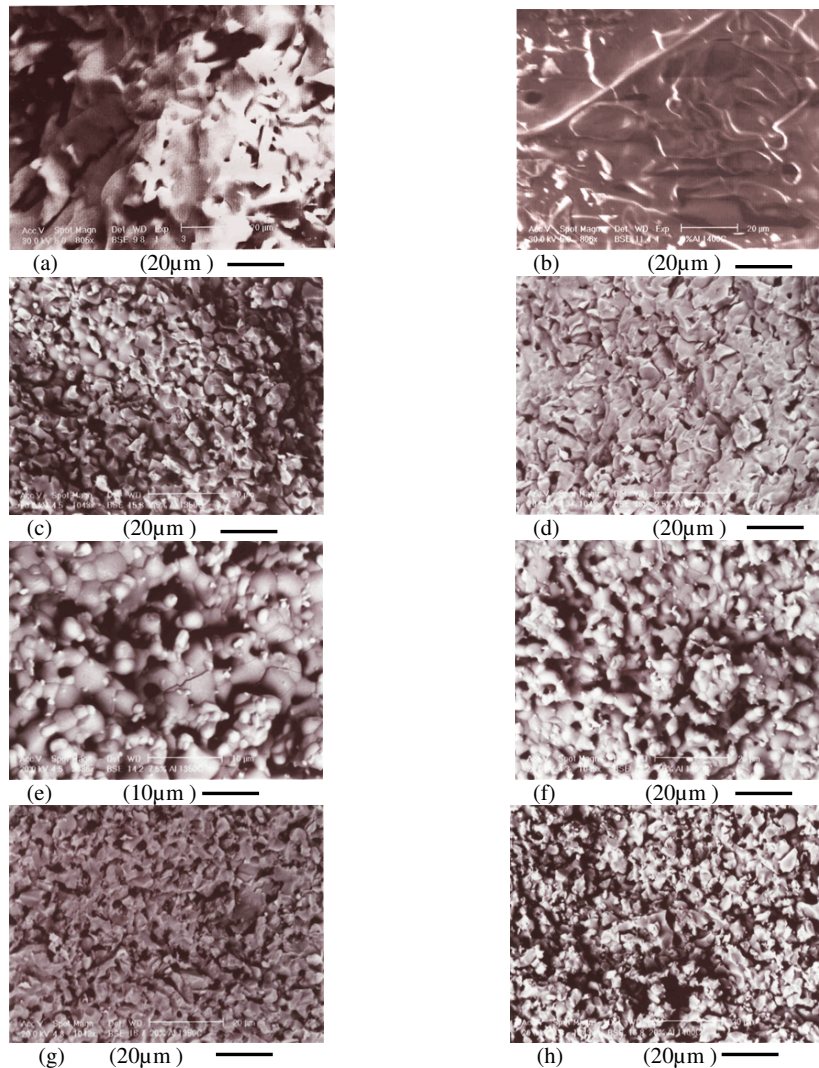


Fig. 5. SEM micrographs of CTCP–26.52 wt% Fap composites sintered without and with different percentages of alumina at various temperatures: (a) 1350°C, (b) 1400°C, (c) 1350°C-2.5 wt%, (d) 1400°C-2.5 wt%, (e) 1350°C-2.5 wt%, (f) 1400°C-7.5 wt%, (g) 1350°C-20 wt%, (h) 1400°C-7.5 wt%.

After sintering, the samples have been characterized by ^{31}P and ^{27}Al MAS-NMR (respectively Fig. 6. and Fig. 7). This analysis shows the evolution of the local environment of the aluminium and phosphorus atoms during the sintering process. Therefore, ^{31}P and ^{27}Al MAS-NMR would be used to study the reactions and interactions between β -CTCP, Fap and Al_2O_3 .

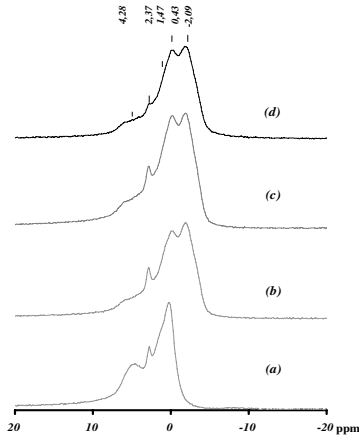


Fig. 6. ^{31}P MAS-NMR spectra of β -CTCP–26.52 wt% Fap composites sintered 1400°C and with different wt% Al_2O_3 : (a) 0 wt% Al_2O_3 , (b) 2.5 wt% Al_2O_3 ; (c) 5 wt% Al_2O_3 (d) 20% wt% Al_2O_3 .

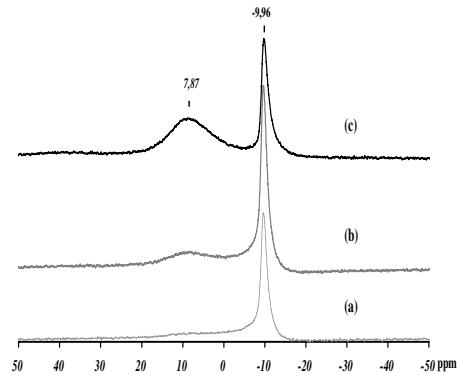


Fig. 7. ^{27}Al MAS-NMR spectra of β -CTCP–26.52 wt% Fap composites sintered 1400°C and with different wt% Al_2O_3 : (a) 2.5 wt% Al_2O_3 , (b) 5 wt% Al_2O_3 ; (c) 20 wt% Al_2O_3 .

The ^{31}P MAS-NMR spectra of β -CTCP–26.52 wt% Fap composites sintered at 1400°C with different percentages of alumina (2.5 wt%, 5 wt% and 20 wt%) are reported in Fig. 6. The ^{31}P MAS-NMR spectra show picks relatives to β -CTCP and Fap. Exceptionally, an intense peak at -2.09 ppm is assigned to the tetrahedral P sites.

The ^{27}Al MAS-NMR spectra of the β -CTCP–26.52wt% Fap composites sintered at 1400°C with different percentages of alumina (2.5 wt%, 5 wt% and 20 wt%) reveal the presence of octahedral Al sites (-9.96 ppm) (Fig. 7.). The intense peak at -9.96 ppm is relative to $\text{Al}(\text{OP})_6$ octahedral sites. The small signal detected around 6 – 15 ppm are related to Al_2O_3 additives phase in the composites, which assigne the presence of octahedral sites.

The biphasic calcium phosphate (β -CTCP–Fap) has excellent biocompatibility but it's low density and the poor mechanicals properties restraints it's use in many load-carrying applications. Alumina has been used in the β -CTCP–Fap composites for its higher stability and its better densification and mechanical properties than β -CTCP and Fap. So, Al_2O_3 additive was used for the β -CTCP–26.52 wt% Fap composite densification. The alumina added with 2.5wt% improves the density and the mechanical properties. Those results were observed when few quantities of alumina where added (from 2.5wt% and 5wt%). Many other studies, such as Hap-alumina- CaF_2 composite proves the interaction and the obtained bodies reached full densification possessing enhanced mechanical properties [19, 23].

4. Conclusion

Ceramic composite containing CTCP-Fap and alumina were successfully obtained at 1350°C . Thus, it was demonstrated that alumina is a promising material for the reinforcement of calcium phosphate. This comparison between samples which is different weight ratio of alumina demonstrates that alumina added with 2.5 wt% improves the densification and ameliorate the mechanical properties when the β -CTCP–26.52wt% Fap composites were sintered at 1400°C . The rupture strength reaches maximum 13.6 MPa at 1350°C when 5 wt% Al_2O_3 are added. At 1400°C , the XRD analyses showed a difference in intensity for each Fap's peaks, with much weaker intensities after

adding 20 wt% of Al_2O_3 . The partial decomposition of Fap in the presence of Al_2O_3 is probably explained as formation of TCP and new phases (CaAl_2O_4). At 1400°C , the ^{27}Al MAS-NMR reveal the formation of new environment assigned probably to $\text{Al}(\text{OP})_6$ octahedral sites. High weight percentage of alumina added to the biomaterial will affect the general properties because its pronounce decomposition when the samples would be sintered. In fact, the density and mechanical properties were influenced by these changes in microstructure and the formation of a large pore. The best condition for the composite densification is probably the adding of few quantities of alumina to improve the density and mechanical properties.

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